Commercial Biodiesel Production

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The biodiesel reaction

- **Produced by a chemical reaction between methanol (or ethanol) and an oil or fat.**
- **100 lb Soybean oil + 10 lb methanol**

  ➔100 lb biodiesel + 10 lb glycerin
- **Requires a catalyst**

(such as caustic soda)

Inputs Used in Biodiesel Production

- Triglygeride or fats and oils – vegetable oils, animal fats, greases, soapstock, etc.
- Alcohol – methanol or ethanol (44% more ethanol is required for reaction)
- Catalyst – sodium hydroxide, potassium hydroxide, sodium methoxide)
- Neutralizer (sulfuric, hydrochloric, or phosphoric acid)

Hydroxide catalysts

- Sodium and potassium hydroxides are popular catalysts due to their low cost.
- They form methoxide (or methylate) and water when combined with methanol.

  $NaOH + CH_3OH \rightarrow NaOCH_3 + H_2O$
- This corresponds to 0.45 g H_2O/g NaOH.
- The water formed can contribute to soap formation.

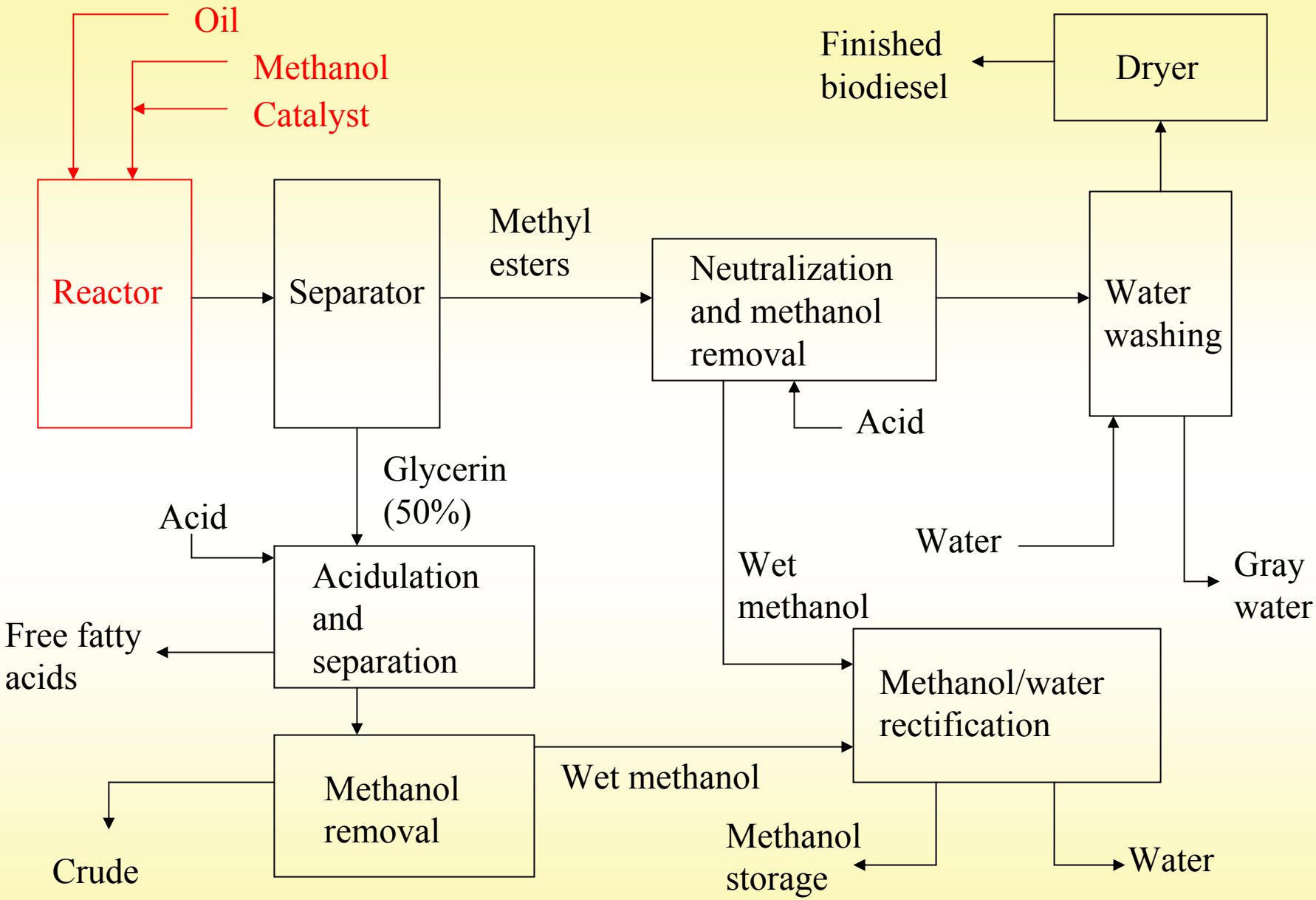
Heterogeneous catalysts

- Standard practice in petroleum industry.
- Currently becoming available for biodiesel, both for esterification and transesterification.
- Offer the potential for clean glycerin.
- Cost-benefit analysis is key.

Relation between feedstock and processing

- The primary differences between feedstocks will be saturation level, free fatty acid level, and water content.
- All feedstocks should be dried to control water.
- Feedstocks with high free fatty acids cannot be transesterified with alkali catalysts (methoxides, hydroxides) due to excessive soap formation. Special pretreatment is needed.

Biodiesel from a saturated feedstock



Biodiesel Production Schematic

Consider only transesterification

- **The reaction is reversible.**

Triglycerides + methanol → biodiesel + glycerin

- **As long as we have excess methanol present, we are forcing the reaction to the methyl ester side.**

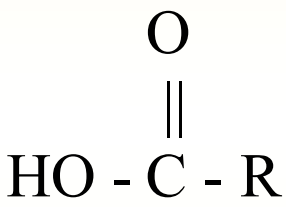
Start with a detailed look at the reaction processes.

Reaction time

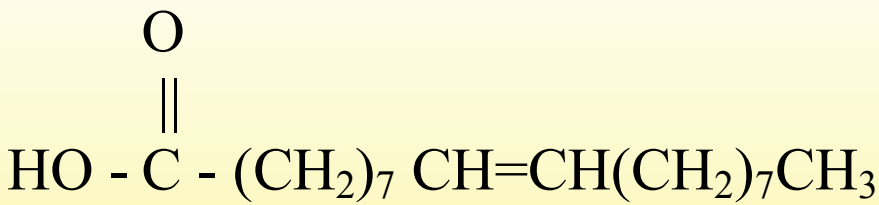
- Transesterification reaction will proceed at ambient (70°F) temperatures but needs 4-8 hours to reach completion.
- Reaction time can be shortened to 2-4 hours at 105°F and 1-2 hours at 140°F.
- Higher temperatures will decrease reaction times but require pressure vessels because methanol boils at 148°F (65°C).
- High shear mixing and use of cosolvents have been proposed to accelerate reaction.

Competing Reactions

- **Free fatty acids are a potential contaminant of oils and fats.**

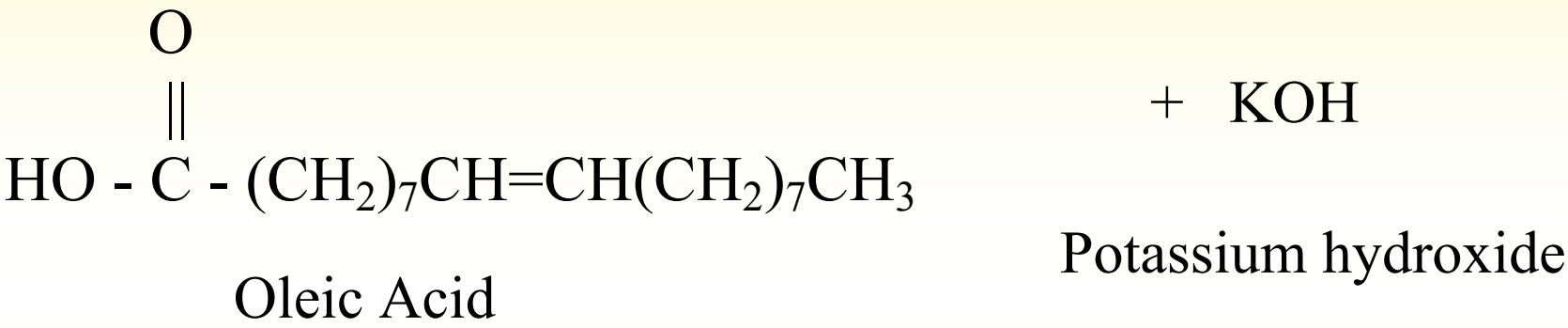


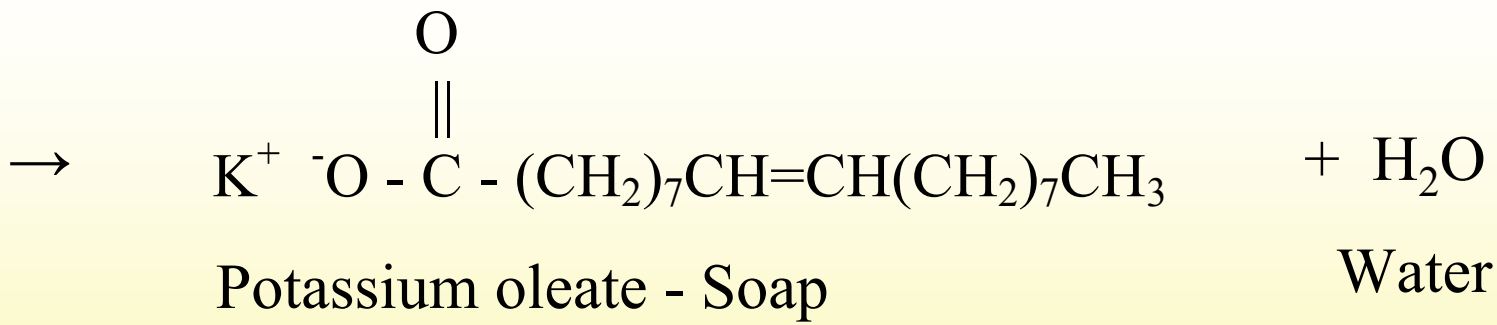
Carboxylic Acid (R is a carbon chain)



Oleic Acid

Fatty acids react with alkali catalysts to form soap.

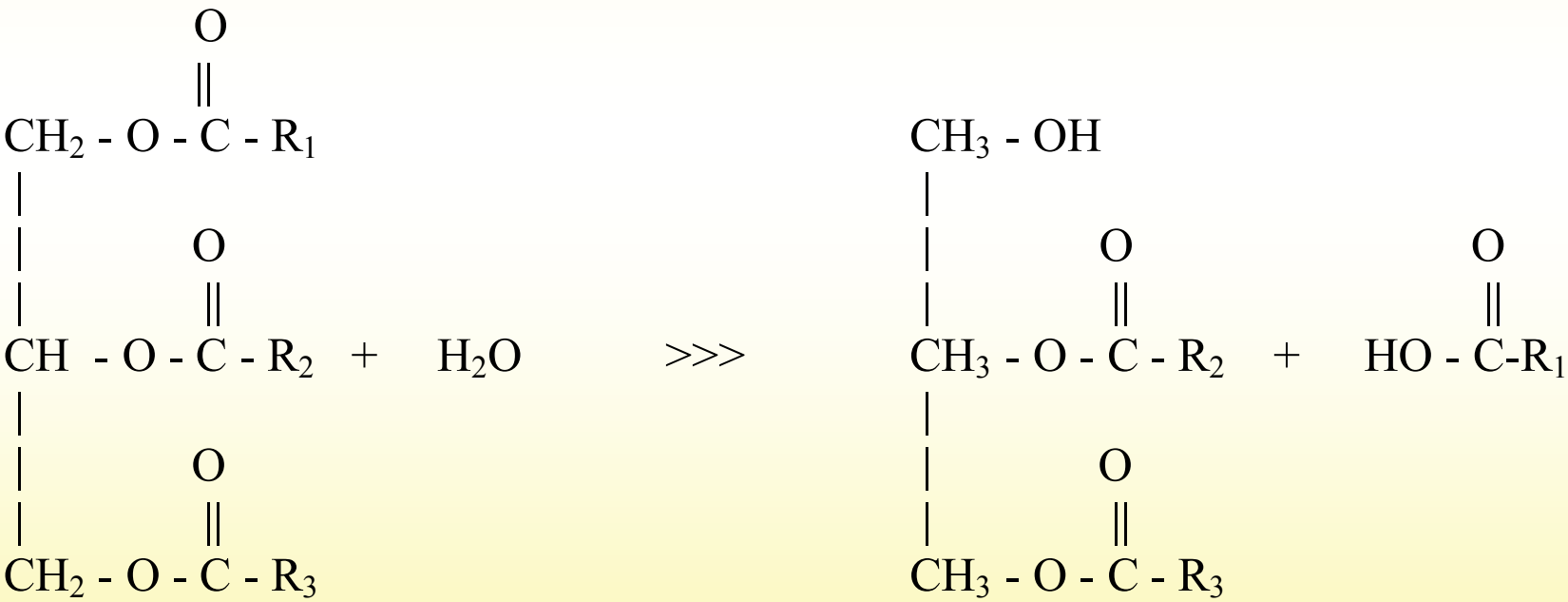




Note that water is a product.

Water is also a problem

Water hydrolyzes fats to form free fatty acids, which then form soap.



Triglyceride **Water** **Diglyceride** **Fatty acid**

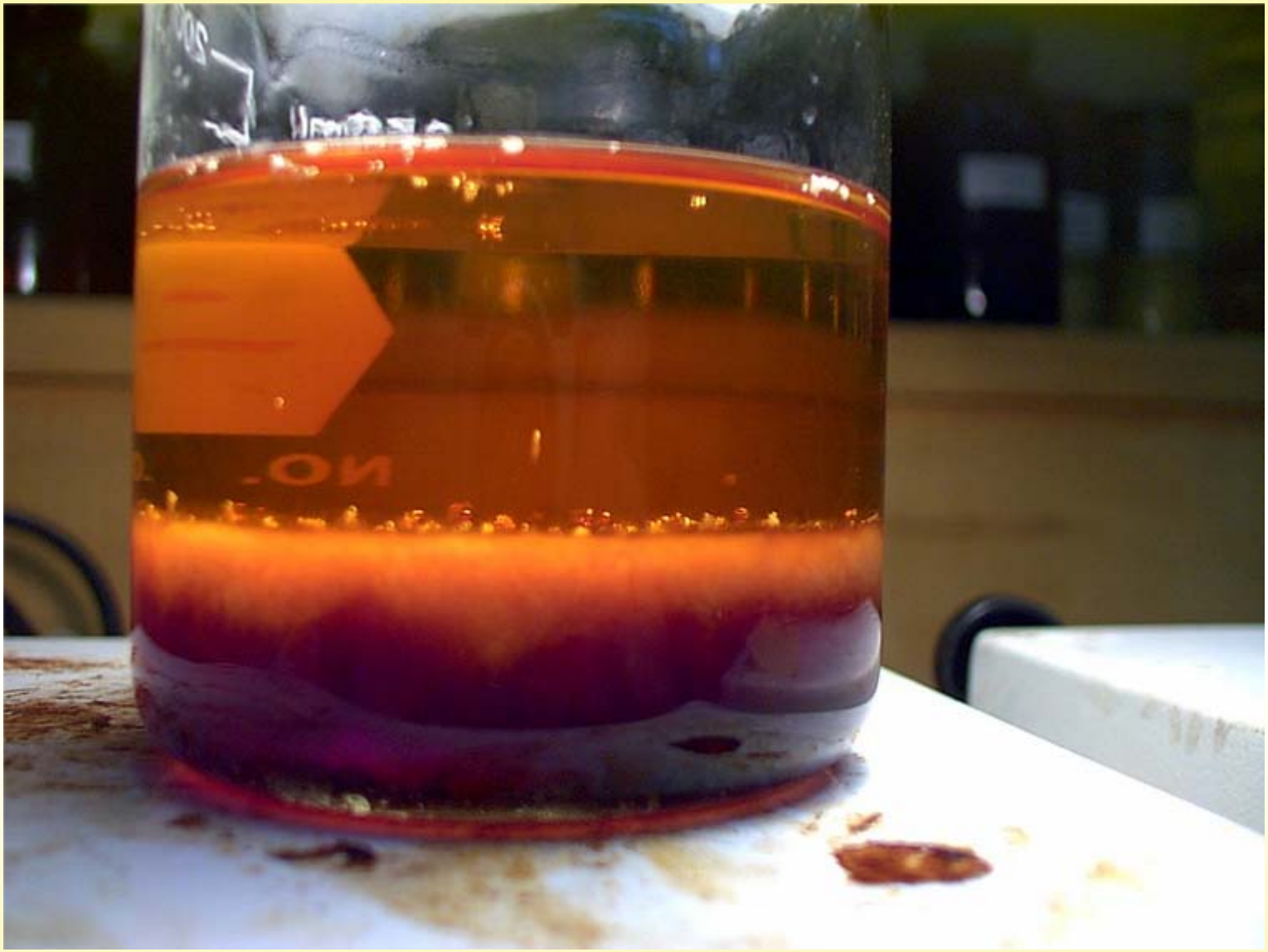
Soap

- Soaps can gel at ambient temperature causing the the entire product mixture to form a semi-solid mass.
- Soaps can cause problems with glycerol separation and washing.
- Soaps can be split by acidulation.

Soap

- Methanol acts as a co-solvent to keep soap in solution with the methyl esters.
- Physical appearance: Usually clear, very viscous
- High soap levels will cause high Sulfated Ash in biodiesel
- High FFA and water often go together (i.e trap grease, restaurant waste). Both contribute to soap formation.

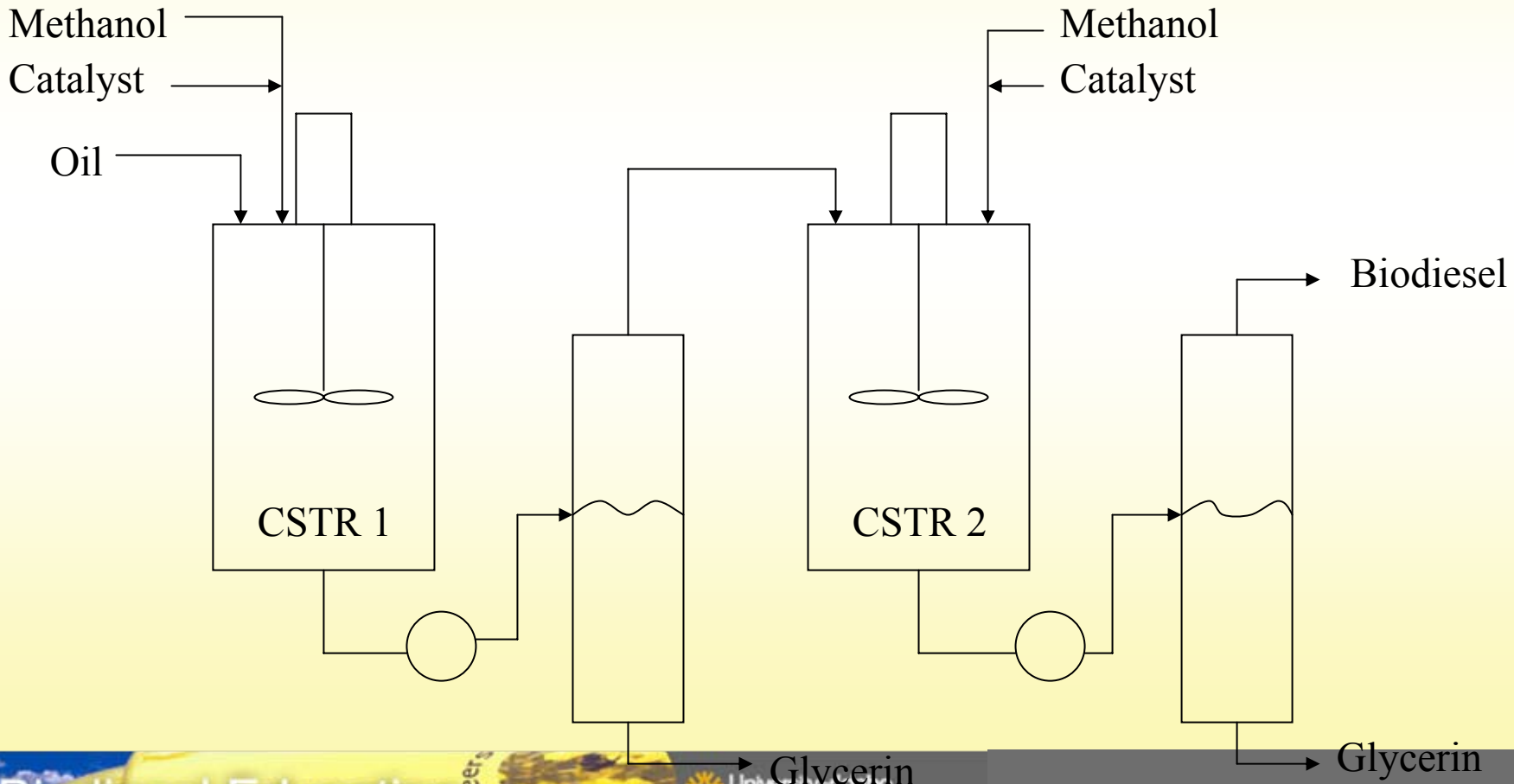
Soap usually appears as a gel or “slime”



Monoglycerides, not soap

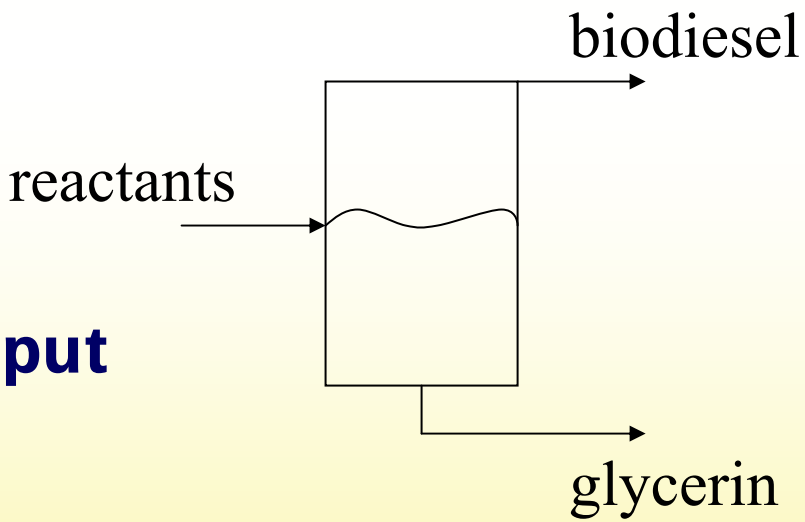
Reactors

- To get a complete reaction requires two or more CSTRs in series.



Biodiesel / Glycerin separation

- **Decanter**
  - **S.G. glycerin = 1.05 (glycerin is 1.26, but here it is mixed with methanol)**
  - **S.G. biodiesel = 0.88**
- **Centrifuge**
  - **High volume throughput**



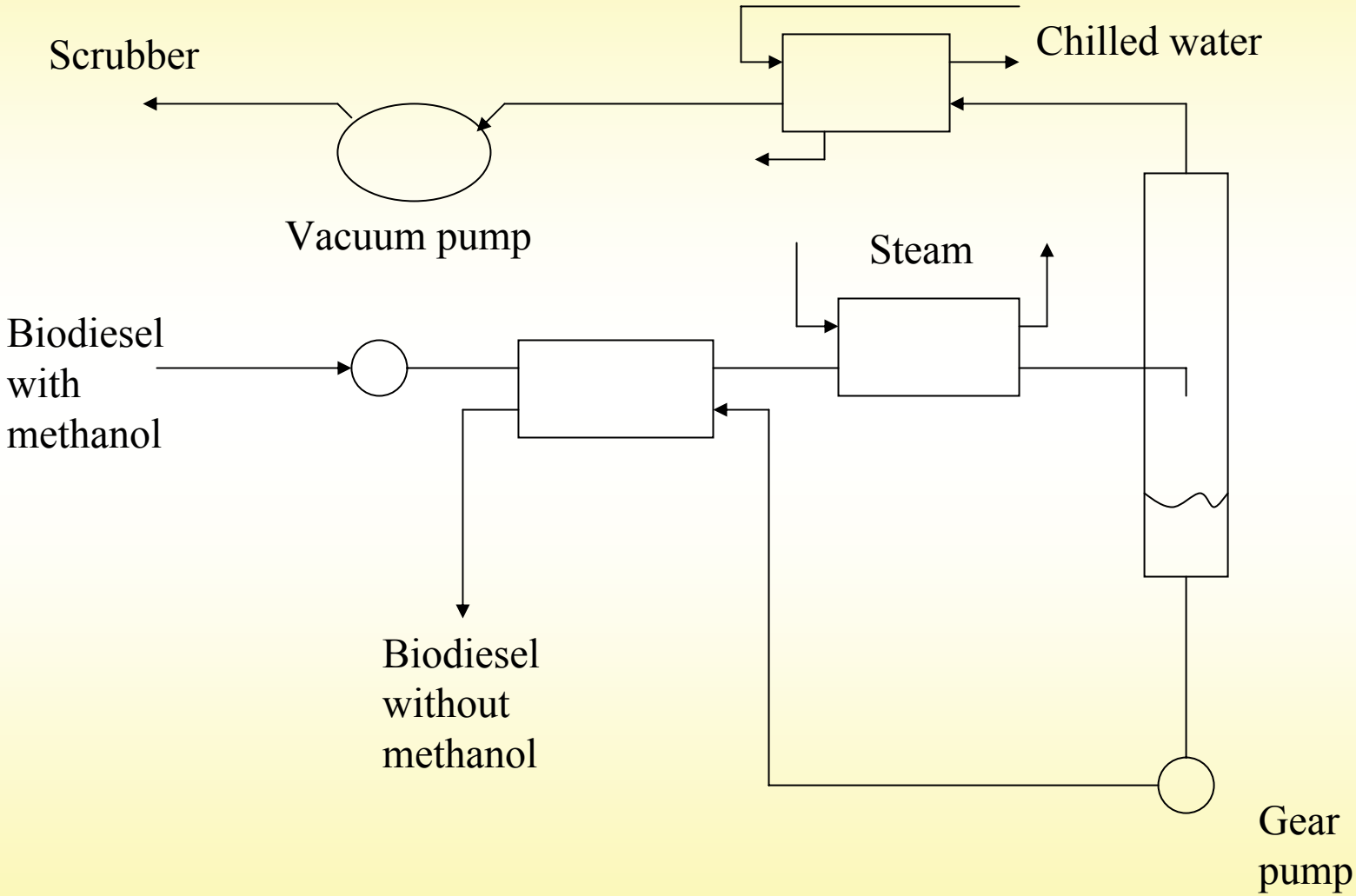
Acidulation / neutralization

- Soaps can be split into free fatty acids and salt by acidulation.

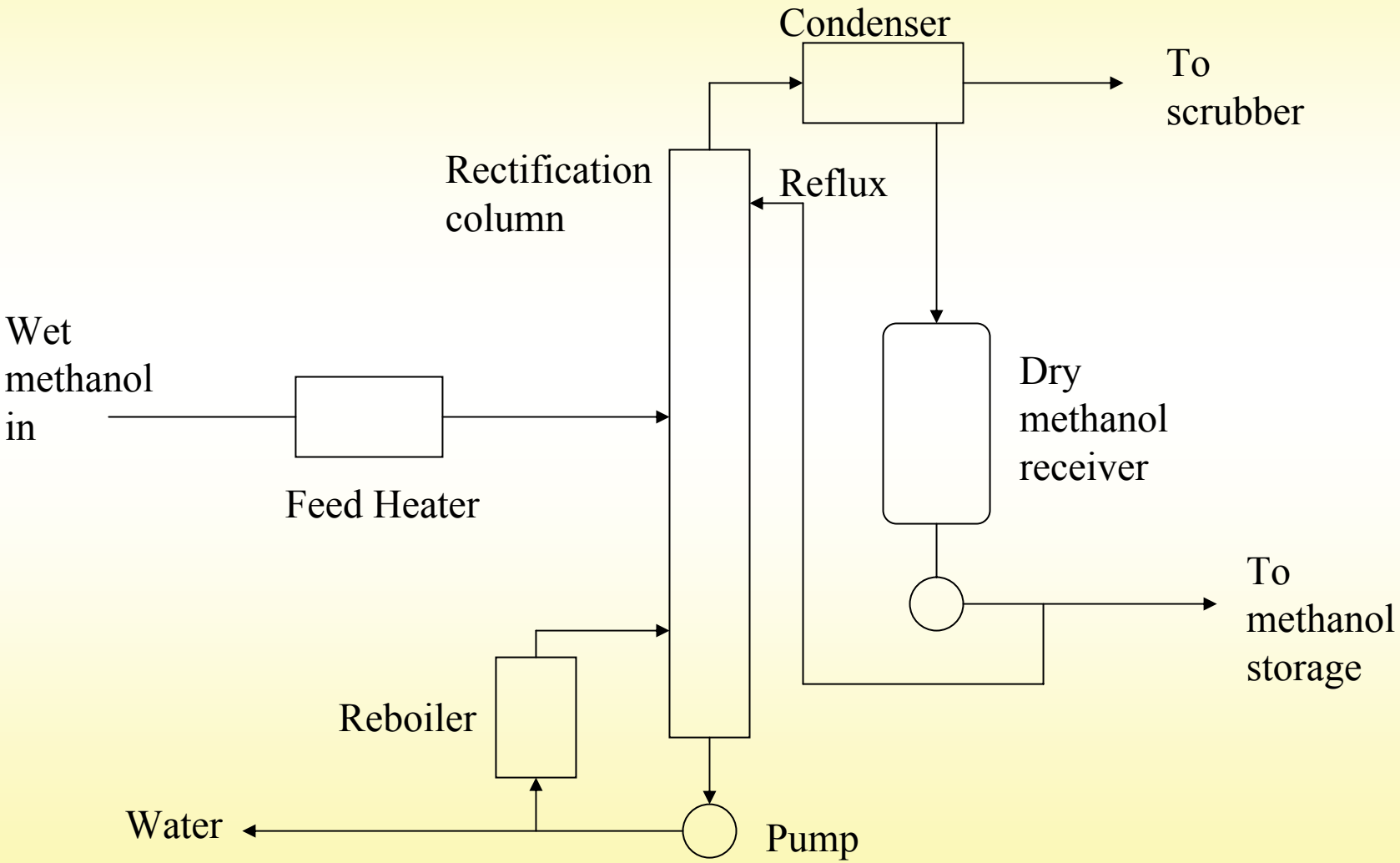
$$\text{Soap} + HCl \rightarrow \text{FFA} + NaCl\ (\text{salt})$$

Eliminating soap can lessen the tendency to form emulsions during washing.

Flash Vaporization of Methanol



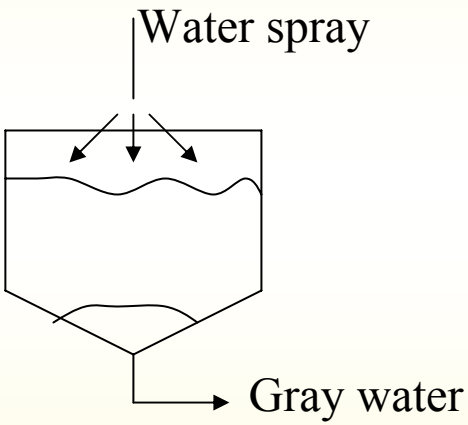
Methanol-water rectification



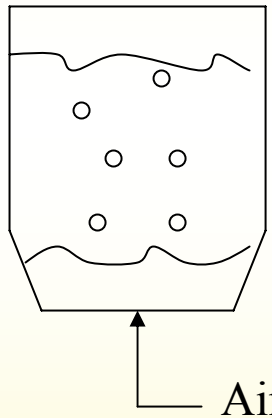
Water washing

- Need to remove contaminants such as soap, residual methanol, free glycerin, and catalyst.
- Use softened, hot water (both the biodiesel and water at 60°C).
- Want to encourage contact between the biodiesel and water with “gentle” agitation to avoid emulsions.
- Acid is often included in wash processes to split soaps.

Washing options

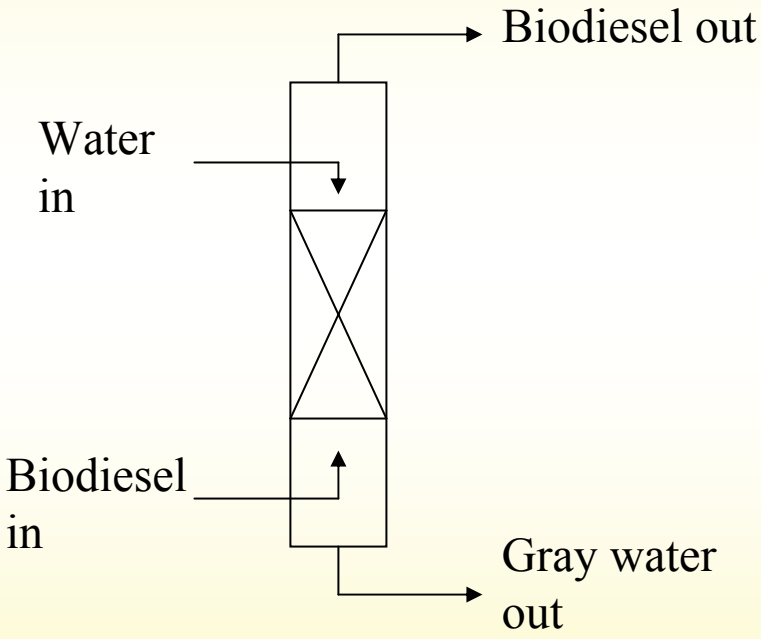


Top spray

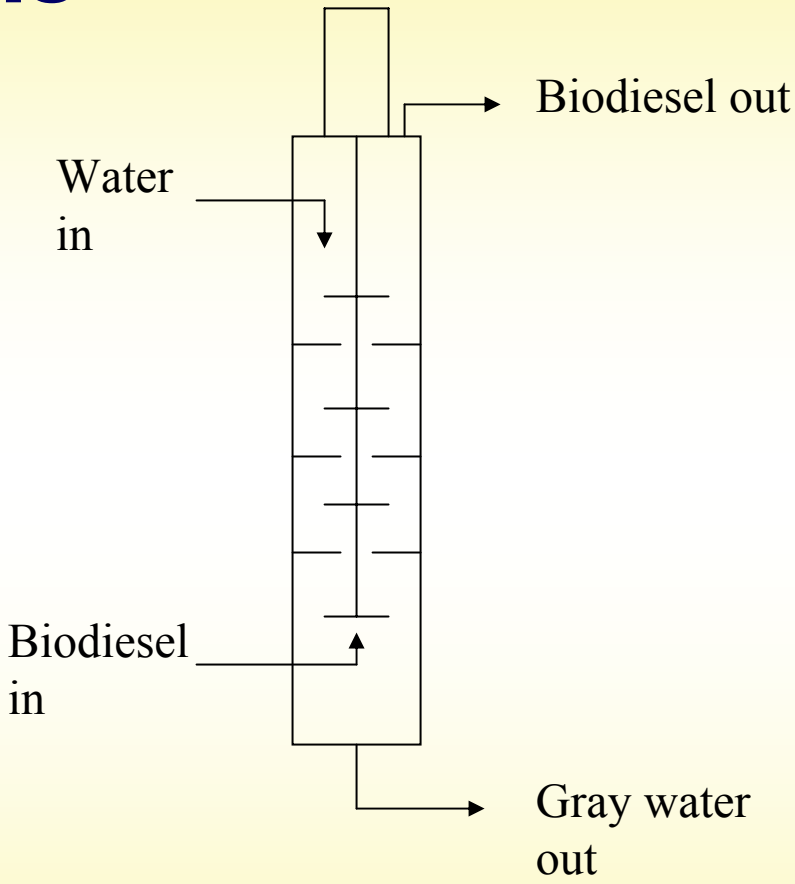


Air bubble agitation

Washing options



Counter flow wash column (with or without packing)



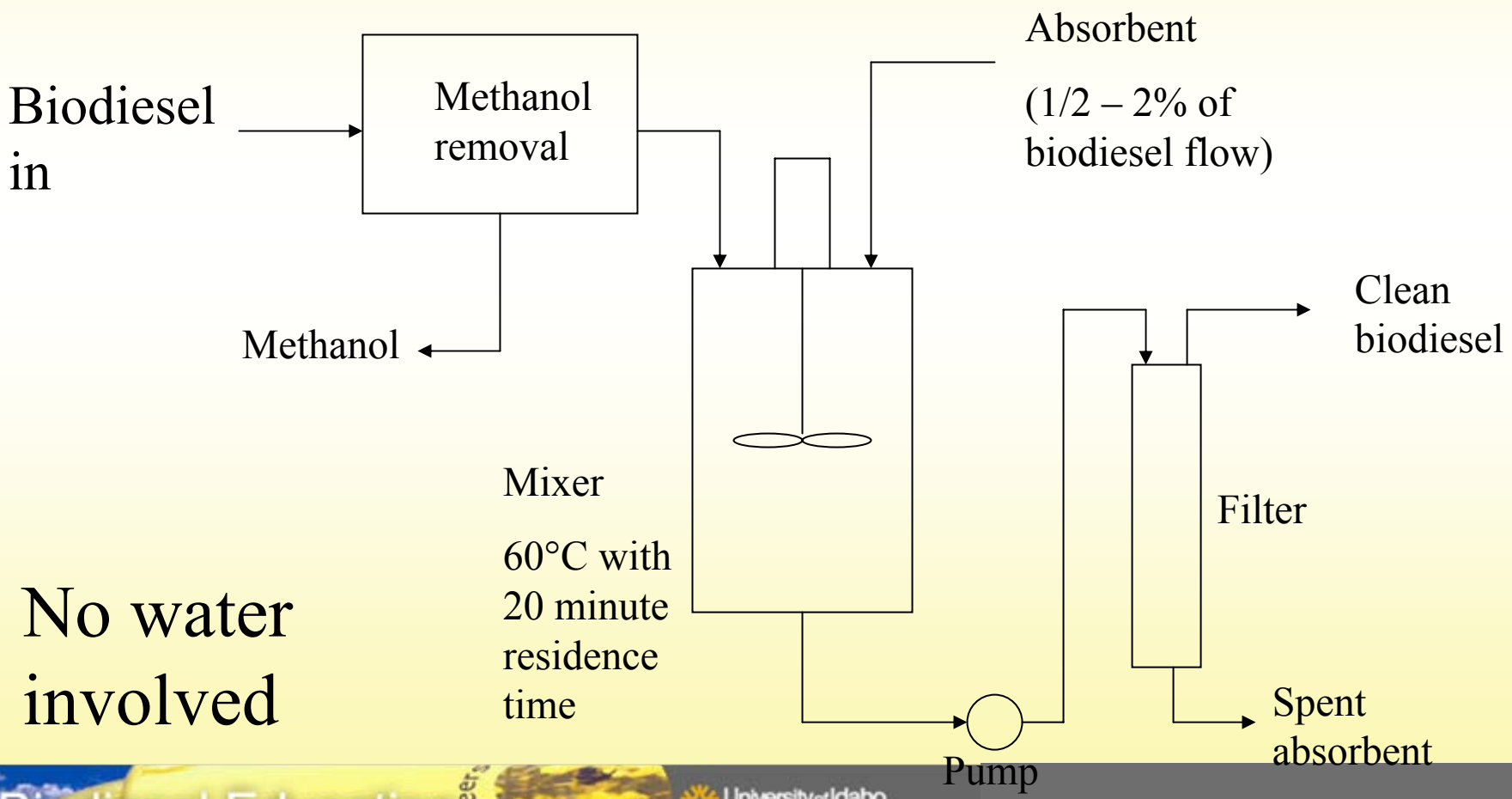
Rotating disk extractor

Alternative to Water Washing

- Water washing is the most problematic step in biodiesel production. It requires heated, softened water; waste water treatment; water/methanol separation.
- An alternative is use of absorbent materials such as magnesium silicate (Magnesol – Dallas Group).

Absorbents

- Can use mixing tank or packed bed.

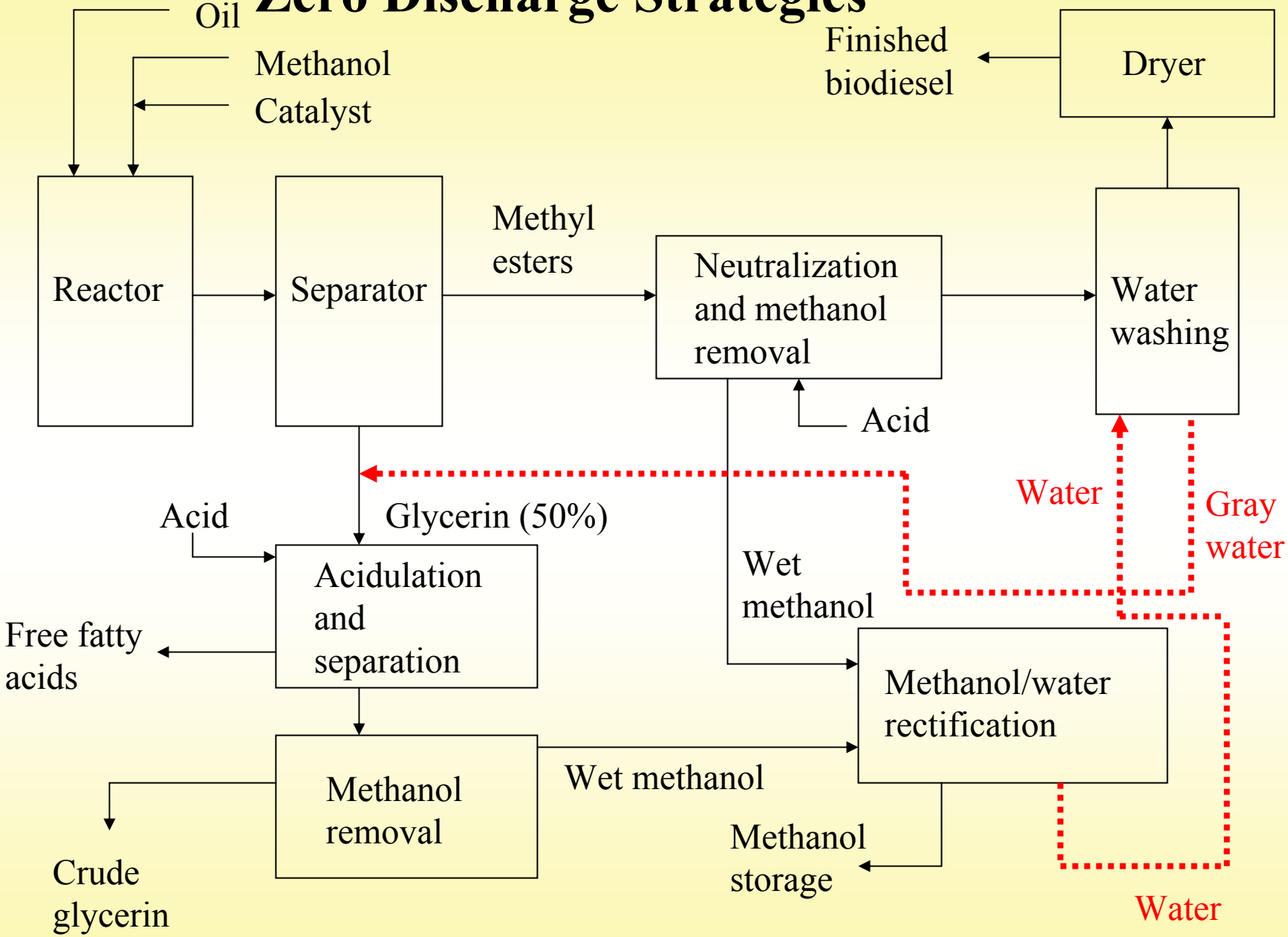


No water involved

Zero Discharge Strategies

- Wash water can have high B.O.D.
- Glycerol is a by-product that can be hard to dispose of. The current market for crude glycerin is limited.
- Discharge streams may require permits and increase regulatory scrutiny.

Zero Discharge Strategies



Glycerin

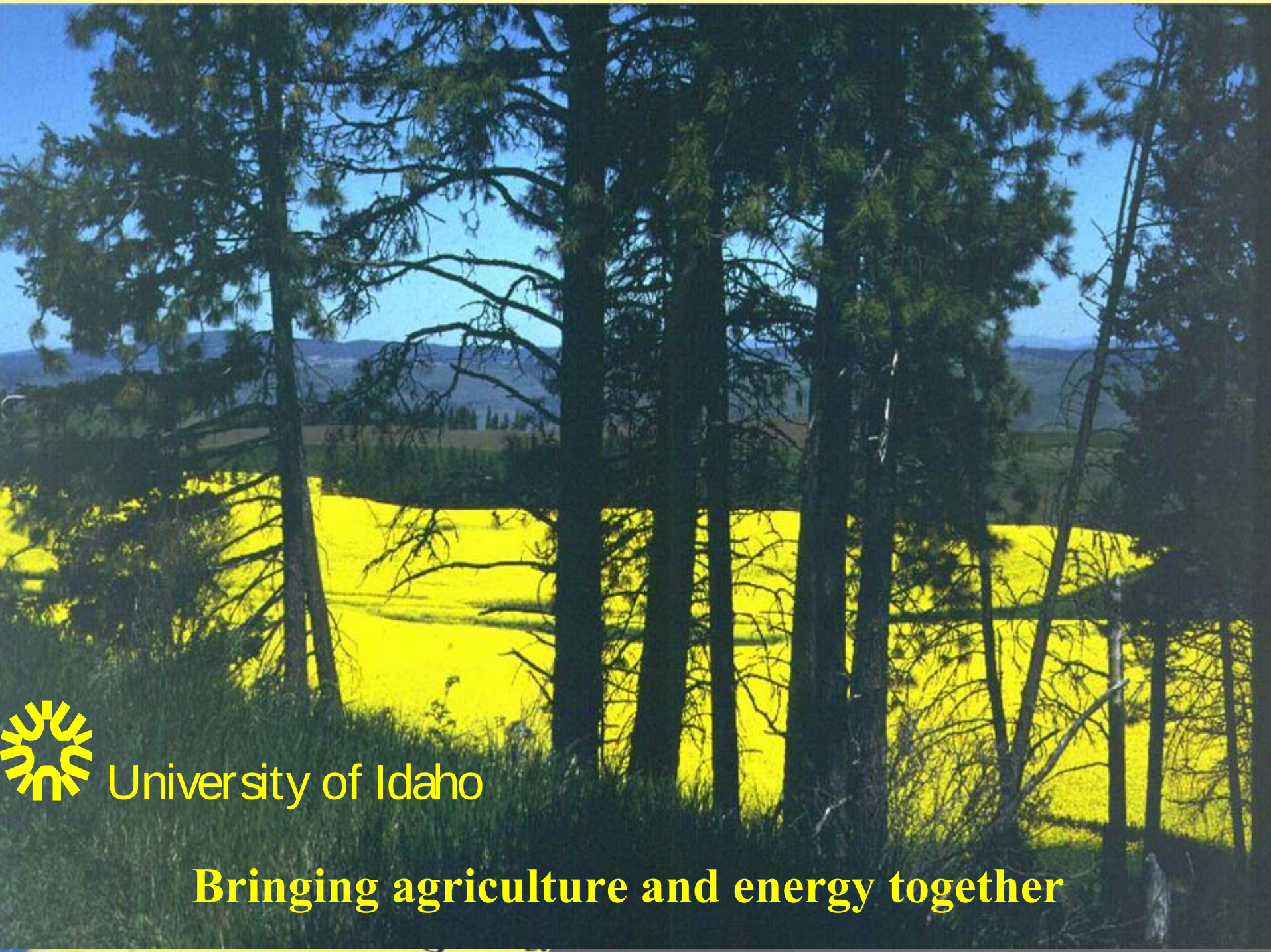
- Don’t assume market will be there. Find a customer early.
- As a commodity product, must be very pure (99.5+%). Kosher approval is also an issue for many markets.
- Glycerin leaving separator is usually only 50% glycerol/40% methanol/10% soap&catalyst.
- Most biodiesel plants can get the glycerin to 80% easily.

Batch vs Continuous Flow

- Batch is better suited to smaller plants (<1 million gallons/yr).
- Batch does not require 24/7 operation.
- Batch provides greater flexibility to tune process to feedstock variations.
- Continuous allows use of high-volume separation systems (centrifuges) which greatly increase throughput.
- Hybrid systems are possible.

Further information

- www.BiodieselEducation.org
- www.me.iastate.edu/biodiesel
- www.biodiesel.org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